Chemical Equilibrium

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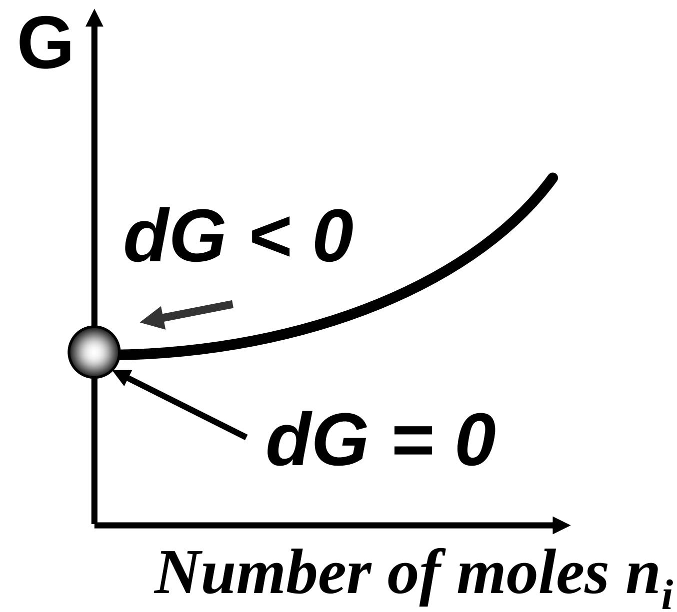
Chemical potential

- The Gibbs function has been shown to be:

$$G = \sum_{i=1}^{C} n_i \mu_i$$

- And the condition for equilibrium takes the form:

$$dG|_{T,P} = \sum_{i=1}^{C} \mu_i dn_i = 0$$



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Ideal gas mixture

- The enthalpy and entropy of an ideal gas mixture are:

$$H = \sum_{i=1}^{C} n_i \bar{h}_i(T) \qquad S = \sum_{i=1}^{C} n_i \bar{s}_i(T, p_i)$$

- $p_i = y_i p$ is the partial pressure of component i (the pressure that component i will have if it occupies the same volume as the mixture at the same temperature)

The Gibbs function for a mixture of ideal gases

- For each gaseous species i that comprises an ideal gas mixture at constant T and constant P, we have:

$$\bar{g}_i = \bar{h}_i - T\bar{s}_i$$

- Associate a sub-volume v_i with each of the C-components:

$$Td\bar{s}_i = d\bar{u}_i + pd\bar{v}_i \quad \Rightarrow \quad d\bar{s}_i = \bar{c}_{v_i}\frac{dT}{T} + \bar{R}\frac{d\bar{v}_i}{\bar{v}_i}$$

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The Gibbs function for a mixture of ideal gases

$$d\bar{s}_i = \bar{c}_{v_i} \frac{dT}{T} + \bar{R} \frac{d\bar{v}_i}{\bar{v}_i}$$

- The individual volumes $\bar{v}_i$ are the `internal degrees of freedom' which may adjust themselves so that the system attains equilibrium.
- An expression for the molar entropy can be calculated for any ideal gas species occupying volume $\bar{v}_i$ at some temperature T by integrating that volume from some reference state.

The Gibbs function for a mixture of ideal gases

$$d\bar{s}_i = \bar{c}_{v_i}\frac{dT}{T} + \bar{R}\frac{d\bar{v}_i}{\bar{v}_i}$$

- Introduce $\bar{v}_i^{ref}$: the volume that a mole of isolated gas would occupy at some temperature T and some reference pressure P^{ref}.
- Integrate from $\bar{v}_i^{ref}$ to $\bar{v}_i$ with constant T:

$$\bar{s}_i(\bar{v}_i) - \bar{s}_i(\bar{v}_i^{ref}) = \bar{R}\ln\frac{\bar{v}_i}{\bar{v}_i^{ref}}$$

The Gibbs function for a mixture of ideal gases

$$\bar{s}_i(\bar{v}_i) - \bar{s}_i(\bar{v}_i^{ref}) = \bar{R} \ln \frac{\bar{v}_i}{\bar{v}_i^{ref}}$$

- Since for an ideal gas:

$$\frac{\bar{v}_i}{\bar{v}_i^{ref}} = \frac{p^{ref}}{p_i}$$

- We conclude: $\bar{s}_i(\bar{v}_i) - \bar{s}_i(\bar{v}_i^{ref}) = \bar{R} \ln \frac{p^{ref}}{p_i} = \bar{R} \ln \frac{p^{ref}}{y_i p} =$

$$= -\bar{R} \ln \frac{y_i p}{p^{ref}}$$

where, the partial pressure of component i is:

$$p_i = y_i p$$

The Gibbs function for a mixture of ideal gases

$$\bar{s}_i(T,P) = \bar{s}_i^0(T) - \bar{R}\ln\frac{y_i\,p}{p_{ref}}$$

- Here $p_i = y_i p$ is the partial pressure of component i – the pressure that the component i will have at temperature T occupying the mixture volume.

$$pV = n\bar{R}T,\ p_iV = n_i\bar{R}T \Rightarrow \frac{p_i}{p} = \frac{n_i}{n} = y_i$$

Chemical potential of component i

$$\mu_i = \bar{g}_i(T, p_i) = \bar{h}_i(T) - T\bar{s}_i(T, p_i)$$

$$G = \sum_{i=1}^{C} n_i \bar{g}_i(T, p_i)$$

Chemical potential of component i

$$\mu_i = \bar{h}_i(T) - T\bar{s}_i(T,P)$$

$$= \bar{h}_i(T) - T(\bar{s}_i^{0}(T) - \bar{R}\ln\frac{y_i\,p}{p_{ref}})$$

$$= \bar{h}_i(T) - T\bar{s}_i^{0}(T) + \bar{R}T\ln\frac{y_i\,p}{p_{ref}}$$

$$= \bar{g}_i^{0}(T) + \bar{R}T\ln\frac{y_i\,p}{p_{ref}} (ideal\,gas\;only)$$

Consider a general reaction

- For a reaction given by:

$$\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D$$

- The equation of reaction equilibrium is:

$$-\frac{\Delta G^0}{\overline{R}T} = \ln K(T)$$

$$K(T) = \frac{y_C^{\nu_C} y_D^{\nu_D}}{y_A^{\nu_A} y_B^{\nu_B}} \left(\frac{p}{p_{ref}}\right)^{\nu_C + \nu_D - \nu_A - \nu_B}$$

$$\Delta G^0 = \nu_C \overline{g}_C^0 + \nu_D \overline{g}_D^0 - \nu_A \overline{g}_A^0 - \nu_B \overline{g}_B^0$$

$$(computed\ at\ T\ and\ 1\,atm)$$

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Example

- Consider the following gaseous reaction:

$$CO + H_2O \longleftrightarrow H_2 + CO_2$$

- Initially we have 2 moles of H_2O and 1 mole of CO_2.
- How many moles of oxygen exist at equilibrium?
- If the reaction is carried out at a different pressure, how will the concentration of CO vary?

Example

- Write the reaction as a sum of 2 reactions!

$$CO + H_2O \longleftrightarrow H_2 + CO_2$$

$$CO + 1/2\ O_2 \longleftrightarrow CO_2$$

0 moles 0 moles 1 mole (initially)

2Y moles Y moles 1-2Y (at equilibrium)

$$H_2O \longleftrightarrow ½\ O_2 + H_2$$

2 moles 0 moles 0 moles (initially)

2-2X moles X moles 2X (at equilibrium)

Example

- Note the mole fractions in the mixture
  - CO: 2Y/(3+X+Y)
  - CO_2:(1-2Y)/(3+X+Y)
  - H_2:2X/(3+X+Y)
  - O_2: (X+Y)/(3+X+Y)
  - H_2O: (2-2X)/(3+X+Y)

$$\begin{array}{ccccccc} H_2O & \rightleftharpoons & \frac{1}{2}O_2 & + & H_2 & -\Delta\overline{G^{rxn}_{H_2O}} \\ CO & + & \frac{1}{2}O_2 & \rightleftharpoons & CO_2 & \Delta\overline{G^{rxn}_{CO_2}} \\ \hline \end{array}$$

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \quad \Delta\overline{G^{rxn}_{CO_2}} - \Delta\overline{G^{rxn}_{H_2O}}$$

Solve for x and y

$$\frac{\frac{2X}{3+X+Y}\left(\frac{X+Y}{3+X+Y}\right)^{1/2}}{\frac{2-2X}{3+X+Y}} = e^{-\left(\frac{-\Delta\overline{G^{rxn}_{H_2O}}}{RT}\right)}$$

$$\frac{\frac{1-2Y}{3+X+Y}}{\frac{2Y}{3+X+Y}\left(\frac{X+Y}{3+X+Y}\right)^{1/2}} = e^{-\left(\frac{\Delta\overline{G^{rxn}_{CO_2}}}{RT}\right)}$$

Example

- A gaseous mixture with a molar analysis of 20% CO_2, 40% CO and 40% O_2 enters a heat exchanger and is heated at constant pressure. An equilibrium mixture of CO_2, CO, and O_2 exits at 3000 K, 1.5 bar. Determine the molar analysis of the exiting mixture.

$$0.2CO_2 + 0.4CO + 0.4O_2 \rightarrow \alpha CO_2 + \beta CO + \gamma O_2$$

Example

$$0.2CO_2 + 0.4CO + 0.4O_2 \rightarrow \alpha CO_2 + \beta CO + \gamma O_2$$

- On the basis of 1 kmol of initial mixture, the reaction is as above.
- Writing equations for the quantities of each element present reduces the coefficients as follows:

$$C: 0.2 + 0.4 = \alpha + \beta \Rightarrow \beta = 0.6 - \alpha$$

$$O: 2(0.2) + 0.4 + 2(0.4) = 2\alpha + \beta + 2\gamma \Rightarrow 1.6 = 2\alpha + (0.6 - \alpha) + 2\gamma \Rightarrow \gamma = \frac{1-\alpha}{2}$$

Example

$$0.2CO_2 + 0.4CO + 0.4O_2 \rightarrow \alpha CO_2 + (0.6-\alpha)CO + \left(\frac{1-\alpha}{2}\right)O_2$$

- The amount of the mixture is

$$n = \alpha + (0.6-\alpha) + \left(\frac{1-\alpha}{2}\right) = \frac{2.2-\alpha}{2}$$

- At equilibrium, this is just the dissociation reaction for carbon dioxide:

$$CO_2 \Leftrightarrow CO + \frac{1}{2}O_2$$